CANMET

Canada Centre for Mineral and Energy Technology

Centre canadien de la technologie des minéraux et de l'énergie

Metals Technology Laboratories

Laboratoires de la technologie des métaux

Energy, Mines and Resources Canada

Énergie, Mines et Ressources Canada

Canada

THE ENERGY OF OUR RESOURCES · THE POWER OF OUR IDEAS

L'ÉNERGIE DE NOS RESSOURCES · NOTRE FORCE CRÉATRICE

METALS TECHNOLOGY LABORATORIES

91-06268/

PRODUCTION OF INTERSTITIAL-FREE STEELS IN LABORATORY FURNACES - A PROGRESS REPORT

A.R. PALMER

MTL 91-48(TR)

This document is an unedited work prepared primarily for discussion and internal exchange purposes. It does not represent a final expression of the opinion of the Canada Centre for Mineral and Energy Technology (CANMET)

Ce document est un rapport préliminaire et rédigé principalement pour fin de discussion et de documentation interne. Il ne représente nullement l'expression finale de l'opinion du Centre canadien de la technologie des minéraux et de l'énergie (CANMET)

MICROMEDIA

14 pp

CANMET

METALS TECHNOLOGY LABORATORIES
REPORT MTL 91-48(TR)

PRODUCTION OF INTERSTITIAL-FREE STEELS IN LABORATORY FURNACES

A Progress Report

by

A.R. Palmer

ABSTRACT

A method of producing Interstitial Free (IF) steels has been developed using MTL's vacuum (225 kg capacity AVS and 20 kg capacity Balzars) furnaces. The procedure includes selection of charge materials, amount of oxide-bearing material to be added, extent of boiling reaction, and the necessary safety precautions to be taken for safe handling of both furnaces. C and N at 20-30 ppm have been achieved, and a source of reliable C analysis at these low levels have been identified.

Because of a lack of oxygen monitoring and therefore control, at the end of carbon boil, recoveries of alloying elements (Mn, Si, Nb, Al, Ti, B) tended to be variable. Therefore, the next step in fulfilling the objectives of this project, would be to increase the confidence in attaining the specified levels of alloying elements in IF steels.

LABORATOIRES DE LA TECHNOLOGIE DES MÉTAUX
RAPPORT MTL 91-48(TR)

PRODUCTION D'ACIERS À INTERSTICES LIBRE DANS LES FOURNAISES DU LABORATOIRE

par

A.R. Palmer

RÉSUMÉ

Une méthode de production d'aciers IF (interstice libre) a été mise au point dans les fours à vide AVS (capacité 225 kg) et Balzars (capacité 20 kg) du LTM. Elle consiste à choisir les matières de charge, la quantité de matière oxydée à ajouter, l'étendue de la réaction d'ébullition et les mesures de sécurité à prendre pour faire fonctionner les deux fours sans danger. Des teneurs en C et N de 20 à 30 ppm ont été réalisées, et une source de dosage fiable du C à ces faibles concentrations a été trouvée.

Comme le contrôle et, partant, le dosage de l'oxygène à la fin de l'expurgation du carbone laissent à désirer, les teneurs en éléments d'alliage (Mn, Si, Nb, Al, Ti, B) récupérés ont tendance à varier. La prochaine étape pour atteindre les objectifs de ce projet consisterait donc à obtenir avec un niveau de confiance plus grand les teneurs recherchées en éléments d'alliage des aciers IF.

OBJECTIVE

To produce steels which contain less than 30 ppm each of the interstitial elements carbon and nitrogen, together with small amounts of added elements such as manganese, titanium, niobium and aluminum.

BACKGROUND

The deep-drawing properties of thin strip are improved when the contents of the interstitial elements carbon and nitrogen are low. About 30 years ago, the steel sheet being used for automotive pressings contained about 0.08% C [1a], and strip with as much as 0.15% C was being used for deep-drawing of cup-shapes [1b]. A carbon content of 0.02% was regarded as "extra low". Oxygen-blowing in the Basic Oxygen Furnace to levels below 0.03% C was likely to cause excessive oxidation of the steel but lower carbon levels could be reached in vacuum degassing vessels, where the element was oxidized by oxygen already in solution.

Japanese workers improved upon the Ruhrstahl-Heraeus vacuum degassing equipment by introducing oxygen into the vacuum vessel, in the so-called RH-OB process (where the last two letters stand for "oxygen-blowing"). Heats of steel as large as 250 tonnes which have been blown in the BOF to levels of 0.03% C and 500 to 700 ppm of oxygen can now be treated to reduce the carbon content to 25 ppm in 20 to 25 min.

In Canada, Stelco is now using RH-OB equipment to produce IF steels. Dofasco treats the metal in a tank degasser with the teeming ladle serving as the reaction vessel.

Nitrogen is not removed by a chemical reaction but some is purged out by the vigorous evolution of CO. Steel made in the BOF does not have a high nitrogen content: levels of about 40 ppm are believed to be typical and these are reduced to 30 ppm or a little less in the course of the decarburization under vacuum.

These steels are also referred to as Ultra-Low Carbon steels but the term "Interstitial Free" is preferred because of its inference that the nitrogen content is also very small.

CHEMICAL PRINCIPLES

Carbon is removed by the familiar reaction with dissolved oxygen:

$$\underline{C} + \underline{O} = CO\ (gas)$$

for which an equilibrium constant can be written as follows:

$$K = P_{CO} / a_C \times a_O$$

where a_C is the activity of carbon. (At low concentrations, this is numerically close to the weight per cent.)

Then

$$a_C \times a_O = P_{CO} / K$$

If the activities are based on the 1 wt % standard state on Henry's law line, the value of 1/K is close to 0.002

The reduction of the pressure of CO, through vacuum treatment, should give a lower algebraic product of the two activities. For a given value of 1/K, a higher value of oxygen activity results in a lower carbon activity.

The combination of the carbon and oxygen atoms takes place between adsorbed species at a metal surface, and the energy barriers to the adsorption and desorption processes make it more difficult to reach equilibrium conditions at low pressures. For example, lowering the pressure to about 8 mm Hg should theoretically reduce the product of the activities by a factor of 100, but in practice the factor is usually 10 or less.

The rate of the reaction increases with the available surface area of the liquid metal. In the enclosed refractory vessel of the RH degasser, the liquid is strongly agitated by circulation through the vacuum chamber and is violently broken up by the effects of the generation of CO and the expansion of the injected argon. The reaction then proceeds rapidly. In a laboratory induction furnace, the agitation must be severely restricted, and the carbon is removed very slowly.

NOTE ON THE UNITS OF PRESSURE

The existing gauges are marked in Torr (i.e. mm of mercury) and all pressures in this report are on that scale. Pressures below 1 Torr are given in milliTorr (mTorr) which are the same as micro-metres or microns of mercury.

Note that 1 Torr = 0.133 kPa; 100 mTorr = 13.3 Pa.

PREPARATION OF LABORATORY MELTS

AIR MELTS

A few melts were decarburized in the 225 kg induction furnace in order to determine the lowest level that could be reached in air and to produce low-carbon steel for subsequent remelting and treatment under vacuum. Billet stock which contained about 0.06% C was melted and iron scale was added until the boiling action had died down to a very low rate. In one experiment,

oxygen was blown as a gentle stream on to the surface of the liquid. The lowest carbon content achieved by these methods was about 0.03% (see Table 1).

VACUUM MELTS

Ingots made from the early air melts were remelted in the A.V.S. furnace and allowed to boil at reduced pressure for periods up to 50 min (Table 1: heats V 260 & 265), but it was difficult to get reproducible results below about 0.01% C (100 ppm). In some subsequent tests, the charge was based on low-carbon "bar iron"* together with steel billets (0.06 to 0.07% C) or electrolytic iron (0.0025 to 0.003% C).

In heat V317 a charge of 75% electrolytic iron and 25% bar iron was partly melted in air (to allow for recharging of the platelets of material which do not pack down easily) and the furnace was closed as soon as all of the charge was in the crucible. The electrolytic iron sintered together and formed a bridge, so that liquid in the bottom of the furnace became superheated and burned through the furnace wall. It is now a rule that no charge in this furnace should contain more than 20 kg of electrolytic iron [2]. For all heats from V355 onward, bar iron (Type FE-V) was the only charge material.

A series of experiments was then made in the Balzers furnace, to develop a satisfactory procedure before attempting further melts in the larger furnace. "Bar iron" was used as the charge material.

The metal was melted under argon. Oxygen was added in the form of commercial iron oxide which was first calcined in a muffle furnace to remove moisture and possible contamination by carbonates. The mechanisms for adding alloys to vacuum melts in both furnaces did not operate well with the fine powder. Wrapping it in paper or aluminum foil has obvious disadvantages, and it was found best to add the oxide with the charge in the cold crucible. Later a supply of "specular hematite", a crystalline form of the oxide, was obtained: this had been graded to pass 20-mesh with a minimum of fines and could be added easily through the hopper mechanism in the A.V.S. furnace.

The boiling action usually began at a pressure below 20 Torr . Pumping continued as the boiling subsided. By trial and error it was found that the rate of rise of the pressure, with the pump shut off, was a useful empirical guide to the attainment of the desired carbon level. For instance, in heat V367 which reached a reported carbon content of 32 ppm, the time taken at the end of the reaction for the pressure to rise from 500 to 1000 mTorr was 90 to 100 s.

The volume of Balzers furnace tank is about 500 L. If this is full of CO at a pressure of 1 Torr and an average temperature of 25 degrees Celsius, the weight of the gas

---

* Grade EFP-II (0.008% C) or FE-V (0.005% C), American Metals Corp., Detroit, Mich.

is 0.75 g. This corresponds to 0.32 g of carbon or about 18 ppm in a melt of 18 kg. A pressure rise of 500 mTorr in 1 min implies that carbon is being oxidized at the rate of about 9 ppm/min.

This result is however at least an order of magnitude too high, since the carbon content is reduced from 50 to about 30 ppm in 40 min. The average rate of loss is thus 0.5 ppm/min, and the rate at the end of the reaction would be well below this average. There was no evidence of a measurable leak rate at the time of start-up before each melt and the discrepancy has not been explained, but the method seems to give a good indication that the carbon content is close to the required level.

Recent heats have been made in the A.V.S. furnace from bar iron with sufficient iron oxide added to give an oxygen content well above 500 ppm. The heat weight was restricted to 160 kg in order to allow plenty of freeboard for splashing during the boiling reaction. (Note that 100 g oxide adds about 185 ppm of oxygen to a 160 kg melt). The procedure was similar to that for the small heats and the reaction was judged to be complete when a pressure rise from 400 to 700 mTorr took at least 50 s. (Here again a calculation of the rate of carbon loss gives a figure which is about 10 times too high.) At this stage, the bubbles appeared in the melt only at intervals of 30 s or more. The lowest pressure reached in the Balzers furnace was a little below 100 mTorr ; in the A.V.S. furnace the minimum was 250 mTorr .

In heat V382, the oxide addition was inadvertently omitted before the pressure was lowered. The bath boiled well for about 15 min, evidently using the oxygen in the bar iron (about 120 ppm) and that picked from the walls of the crucible.

When the reaction was judged to be at an end (usually after 50 to 60 min of boiling), electrolytic manganese and ferro-silicon were added through the hopper mechanism, followed by ferro-niobium (where specified), aluminum and titanium.

It is interesting to compare the procedure employed in the Dofasco Research Dept. for making heats of I.F. steel, in the course of developing an industrial process. The raw material was Armco Iron, which was reported to contain 0.01 to 0.02% C and 900 ppm of oxygen. The small pieces of plate were melted in a 100 lb vacuum furnace but bridging was not a problem because the material could be added in small portions through a vacuum lock. Boiling began at about 50 Torr and continued down to 100 milliTorr or a little less in the course of 40 to 60 min, giving final carbon contents as low as 15 ppm.

OXYGEN NEEDED FOR THE REACTION AND ITS EFFECT ON THE FURNACE LINING

During the sequence of heats V379 through 382, it became increasingly difficult to sustain the boiling action. Additions of oxide caused moderate bubbling for a few minutes but the action died down within 10 min and was not stimulated even when the pressure was below

400 mTorr . The time for the "pressure rise" (from 400 up to 700 m Torr) was as long as 80 s. The amount of oxide added was increased from heat to heat.

It appeared that the furnace lining was becoming glazed by reaction with excess oxide and that its efficiency in nucleating CO bubbles was reduced. A "wash" heat of stock billets was made with the intention of dissolving some of the excess oxide (V384). About 1% of silicon was added during and just after the melting step; 0.1% of aluminum was added before the steel was poured. The hot walls were scraped just after the furnace had been emptied and were found to be coated with a pasty material which solidified to a dark, hard and porous clinker.

Heat V385 made a few days later showed a good boiling action for about an hour, without any addition of oxide but the final carbon content was higher than in heats made with oxide additions.

At this point it was felt advisable to install a new lining. The old one had served for 13 heats and was not badly worn, but it was feared that oxide penetration might give rise to weak spots. Pieces of the old lining showed oxide penetration to about 35 mm in the bottom and somewhat less in the sides. This zone was very hard and dense and was difficult to break when cold. At the time of writing, the preliminary results from a mineralogical analysis indicate that the alumina particles in the lining were being converted to hercynite ($FeO.Al_2O_3$) by reaction with the oxidized melts. There is also an intergranular phase of silicate, which was probably added to provide the bond between the particles. Pure hercynite has a melting point of nearly 1800°C. This can be lowered if the compound also absorbs silica, but the amount in the original ramming mix is thought to be too small to cause a drastic reduction of the softening point of the lining.

INTERNAL QUALITY OF THE STEEL

Samples cut from several ingots were polished and examined under the microscope so that the types and quantities of non-metallic inclusions could be observed. The observations are summarised in Table 3.

In general the specimens showed only very small quantities of dispersed dark particles, most of which were smaller than 5 microns in diameter. At high magnifications some of these were seen to be MnS but those of a darker colour appeared to be oxidic. In some specimens, these were somewhat angular and probably consisted of alumina or an aluminate. In heats of low final Al content, the oxides had rounded shapes suggesting silicates. Some of these contained a second, darker phase.

A few specimens contained particles grouped in one or two small clusters which were usually not greater than 60 microns across. Those consisting of somewhat angular (or occasionally, lath-like) particles were probably of alumina but others with more rounded particles were thought to contain an oxide of titanium. Oxides appeared to be slightly more plentiful in heats to which larger amounts of oxide had been added (e.g. V383).

ANALYSIS FOR VERY LOW CARBON CONTENTS

Special precautions were taken in drilling the ingot slices for analysis, in order to avoid traces of oil or fingermarks which could contribute small amounts of carbon. The slice was thoroughly cleaned with alcohol and drilled with a clean bit which was reserved for the purpose. Drillings were collected on clean paper or on aluminum foil.

The ingot samples from heats down to No. V360 were analyzed in the Leco combustion equipment in the Mineral Sciences Laboratories at 555 Booth Street. This is an older model which is not designed to analyze samples containing much less than 0.010% C.

Some samples were submitted to Ortech, Sheridan Park, Ontario but we now understand that an older Leco model was being used there. Drillings from sets of ingots poured from single heats showed fairly wide variations, leading us to believe that the equipment does not provide the level of accuracy required for this type of steel.

Six samples were analyzed by courtesy of Leco Instruments Corporation at its laboratory in St. Joseph, Michigan.

A few samples were analyzed in the Research Department of Dofasco Inc. which has the Leco model suited to these grades of steel. The analyst has conducted extensive tests to ensure accuracy in analyzing the company's own IF steel. Dofasco later agreed to analyze samples on a continuing basis at the Bayshore Laboratory.

Details of the melts are summarized in Table 1, attached.

DISCUSSION

The existing procedure is capable of producing steel with the carbon contents of 25 to 30 ppm. The nitrogen levels are consistently in the same range. There is no measurable loss of that element but the raw material has a content below 30 ppm and there is no pick-up, since all of the melting is done under argon.

We have not yet learned to obtain consistent oxygen levels in the melt at the end of the reaction and the recoveries of manganese, silicon, titanium and aluminum are therefore variable. The low final aluminum contents of some of the recent heats and the fact that the titanium content was much lower in the third ingot than in the first one in some sets together indicate that the final oxygen contents of those melts were too high.

Carbon contents below 30 ppm had been obtained with iron oxide additions of less than 300 g (for the 160 kg heats). It is now thought that additions of 400 g or more in the recent heats were excessive and may have contributed to the conversion of alumina in the lining to hercynite.

The steel produced is generally very clean. Most ingots contain small, well-dispersed particles of unidentified oxides. In a few specimens, small clusters of fine alumina were seen but

neither the single particles nor the clusters were considered to be large enough to give rise to defects in cold forming of thin strip made from the steel.

In future work it is recommended that heats should be allowed to react for 10 or 15 min without any added oxide. About 260 g of hematite ore should then be added in two portions, with perhaps 15 to 20 min of reaction after each, for a total reaction time of 50 to 60 min.

REFERENCES

1. Metals Handbook, 8th. Edition (1961): (a) p 320; (b) p 330.

2. Operating Manual for the A.V.S. Vacuum Furnace: A.R. Palmer and H.-P. Guindon: Report No. MTL 89-21(INT).

Table 1: Early Experiments in making Low-Carbon Steels

Heat No.	Wt. kg.	Date	Raw materials	Additions (g) O-bearing	FeSi	Al	Ti	Boiling time mins.	Ingot Analysis C ppm	N ppm	Mn %	Si %	Al %	Ti %	O ppm	
			I. LOW-CARBON AIR MELTS													
2441	50	Nov'86	Electro I	--	50	35	--	--	20	45	.35	.01	<.005	-	280	for U of T vac. heat V 206
2660	175	May'87	Green bts	scale 450	800	250	--	15	250	23	.08	.09	<.005	-	300+	
2684	185	Jun'87	-"-	02, scale	1000	300	--	22	250	--	.05	--	--	-	--	Ingots porous
2824	190	Jan'88	-"-	scale 640	1000	380	--	6	400	40	.10	.17	.07	-	80	--> V 260
2828	190	Jan'88	-"-	02, scale	800	200	--	20+	380	--	.075	.08	.004	-	--	--> V 265
			II. VACUUM MELTS.													
260	160	Jan'88	Ing.2824 +bar iron	scale 150	600	150	--	29	90	60	.02	.01	<.005	-	370	Melted in air
265	160	Feb'88	Ing. 2828	scale 400	700	180	--	50	160	27	.01	.27	.015	-	70	
314	160	Sep'88	Blts.Barl	scale 700	300	160	--	38	120	32	.18	.12	.016	-	50	Took 1st.test in air
317	160	Nov'88	El.I+Barl	(Burned through crucible)												

Table II: Interstitial-free Steels.

Heat No.	Wt. kg.	Additions (g) Ore	FeSi	Al	Ti	FeNb	Boiling time mins.	INGOT ANALYSIS — Carbon ppm: C'MET	Ortech	LC*	Dofasco	B ppm	Mn %	Si %	Al %	O ppm	Ti % Aim	Ti % Final	Nb % Aim	Nb % Final
							AIMS →		(30			<30	.15	.03	-	<70				
355	16	nil	25	10	10	--	10	90				24	.13	.06	<.005	125	.04	.035	--	--
356	16	25	10	20	15	--	32	300?				--	.20	.08	.012	--	.045	.043	--	--
360	16	12	5	25	15	--	20+	60				23	.23	.06	.027	60	*	.07	--	--
365	18	45	10	25	13	--	55	~60^			55	24	.16	.06	.045	67	.05	.047	--	--
366	18	53	10	25	13	--	48	35	30	36	44	31	.12	.03	.01	92	*	.036	--	--
367	18	25	8	20	15	--	17	34	29		33	29	.14	.03	.030	80	*	.054	--	--
371	18	30	10	18	15	--	35		31	44	41	25	.14	.02	<.005	110	*	.022	--	--
372	18	28	10	30	15	--	32		35	33	26	25	.11	.02	.019	60	.045	.043	--	--
373	18	28	10	30	--	--	40	31	33		32	26	.09	.014	.058	45	--	--	--	--
374	18	28	10	30	--	8	30		58	27	19	28	.08	.012	.010	58	--	--	.0225	.025
375	160	200	90	160	130	--	55		40a	47	38	26	.23	.05	.04	48	.045	.058	--	--
376	160**	270	100	200	145	--	51		27b	26	22	27	.20	.05	.01	52	*	.045	--	--
379	160	375	75	200	--	--	70				20	25	.13	.03	.01	42	--	--	--	--
380	160	400	75	200	--	60	40	37			32	42	.13	.03	.02v	63f	--	--	.0225	.018
381	160	400	75	200	140	14	45				28	34	.12	.026	.01	96f	.045	.045v	.0045	.004
382	160	400	75	200	140	14	42				27	26	.08	.013	<.005	90f	*	.03v	*	--
383	160	440	75	200	145	--	53				25	26	.10	.018	d	k	*	.04v	--	--
385	160	nil	75	250	70	14	62				47	27	.17	.06	.025v	80	.023	.026v	.0045	z

* Leco Corpn., St. Joseph, Mich.
** melted 210 kg, added 180g ore, then poured one ingot.
^ approx. (mean of 48 & 69 ppm).
a mean of 32, 55 and rechecks 30, 41.
b mean of 22, 27, 27 and rechecks 21, 25,40.
d erratic results: <.01 to .045 in each sample.
v average of 1st.& 3rd. ingots.
; Ti added before Al, in error
f wide scatter of results: av.given
h hematite ore (specular) used in this and later heats
k ingot A:50 ppm; B: 1 5 ppm
z result to come.

29 June 1990

Table III: Non-metallic Inclusions in I. F. Steels

Note: Specimens of about 15 x 20 mm in the unetched condition were scanned initially at 100X. Particles of interest were examined at higher magnifications. Sizes of particles and clusters were measured against a scale in the eyepiece (sizes are reported below in microns (i.e. micrometres).

V365: A few elongated grey particles, probably silicates: up to 100 long. Otherwise very clean.

V366: One alumina cluster 600 x 330 (rating of 100) - very fine particles.

V367: No alumina seen: very clean.

V371: Two small clusters of rounded particles (possibly Ti oxide?): larger one was 100 x 70 (rating of 3.5). Otherwise very clean.

V372: A few dark particles of diam. up to 4 or 5; otherwise as V373-4.

V373: Small medium-grey particles, diam <2: maybe silicates?

V374: A few small grey particles - maybe sulphides? (diam. smaller than 3).

V383A-B-C: Small dispersed particles, diam. smaller than 5 in ingot A, up to about 8 in B & C. Some have light-grey colour of MnS, others were darker and round: probably silicates (some enclosing a particle of a darker phase). Specimens from ingots B & C showed one or two very small clusters of alumina (or Ti oxide?). All three had a "background" of extremely fine particles, resolved only with difficulty at 500X.

Etched specimens (2% Nital) showed only larger ferrite grains of irregular outline, some with twin markings. No pearlite was seen.